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Band-gap Engineering in Sputter Deposited Amorphous/Microcrystalline $Sc_xGa_{1-x}N$

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BAND-GAP ENGINEERING IN SPUTTER DEPOSITED AMORPHOUS/MICROCRYSTALLINE $Sc_XGa_{1-x}N$

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Abstract. Reactive sputtering was used to grow thin films of $Sc_xGa_{1-x}N$ with scandium concentrations of 20%-70% on quartz substrates at temperatures of 300-675 K. X-ray diffraction (XRD) of the films showed either weak or no structure, suggesting the films are amorphous or microcrystalline. Optical absorption spectra were taken of each sample and the optical band gap was determined. The band gap varied linearly with increasing Ga concentration between 2.0 and 3.5 eV. Ellipsometry was used to confirm the band gap measurements and provide optical constants in the range 250-1200 nm. ScN and GaN have different crystal structures (rocksalt and wurzite, respectively), and thus may form a heterogeneous mixture as opposed to an alloy. Since the XRD data were inconclusive, bilayers of ScN/GaN were grown and optical absorption spectra taken. A fundamental difference in the spectra between the bilayer films and alloy films was seen, suggesting the films are alloys, not heterogeneous mixtures.

Key words. band-gap engineering, amorphous, III-nitrides, scandium nitride, ellipsometry

Subject Classification. Material science

1. Introduction. Nitride semiconductors have generated much research due to their optoelectronic applications. The ability to form alloys of GaN, InN, and AlN with continuously varying band gaps is one reason for the interest in these materials. By band gap engineering and subsequent creation of heterostructures, devices such as light-emitting diodes, laser diodes, and detectors with widely varying properties can be fabricated. High temperature applications for these devices have lead researchers to look for a replacement for InN (due to its relatively low melting temperature) in these alloys. Calculations by Drabold and Stumm suggest that amorphous GaN may serve as a useful electronic material due to its lack of midgap states [1]. More recently, amorphous $Al_xGa_{1-x}N$ has been grown and shown to have a band gap linearly dependent on the alloy composition [2]. It has also been suggested [3] that ScN, because of its higher melting temperature and lattice spacing match (even though ScN is a rocksalt structure material, not wurtzite) with GaN, may serve as a useful replacement for InN.

Controversy still exists over the direct or indirect nature of the optical gap in ScN. Experimental evidence and theoretical calculations suggest that crystalline ScN has a direct band gap between 2.0-2.4 eV, with 2.1 eV being the most accepted [4-7]. Moustakas, Molnar, and Dismukes [8] reported a fundamental absorption edge at 2.1 eV for polycrystalline ScN but were unable to determine whether the gap was direct or indirect. A much weaker indirect transition between 0.9 and 1.3 eV is predicted [6,7] by band structure calculations. (Our measurements do not extend to low enough energy to investigate this transition). For this paper, we will consider the onset of strong absorption to be the optical band gap. As suggested in reference 3, alloys of ScN and GaN may have optical band

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gaps, which vary between 2.1 and 3.4 eV. We present here experimental evidence that alloys of $Sc_xGa_{1-x}N$ have a linear relationship between the optical band gap and metal composition in the range of 2.0-3.5 eV.

2. Experimental Procedures. Thin films of $Sc_xGa_{1-x}N$ were grown by reactive sputtering in the temperature range 300-675 K. Details of the growth conditions are given in reference 9. Film composition was measured using a JEOL JSM-5300 scanning electron microscope with and Oxford 5508 x-ray detector for energy-dispersive x-ray spectrometry (EDS) measurements. The films were assumed to be stoichiometric. The composition was determined form the ratio of peak areas of Sc and Ga measured with EDS and ranged between 20% and 70%. Film structure was investigated with x-ray diffraction (XRD). A Rigaku powder diffractometer with a two-axis sample stage goniometer was used for these measurements. Optical absorption was measured in the range of 190-820 nm with a Hewlett Packard 8451A diode array spectrophotometer with the beam at normal incidence to the sample. Film optical properties were also measured with a J.A. Woollam Co. variable angle spectroscopic ellipsometer (VASE) with rotating analyzer. Spectra were taken at three angles about the Brewster angle in the range 450-1200 nm. Spectra were fitted using the supplied WVASE software. A Lorentz model consisting of 5-7 oscillators (depending on the sample) was used to model the material.

3. Results and Discussion. Absorption spectra were taken of each film with the HP 8451A. A clear trend toward increasing band gap with increasing gallium concentration was seen [9]. For all films, making a linear fit to the absorption squared in the strong absorption region provided a rough estimate of the optical band gap. The intercept of this line and the energy axis then defines the "gap" (as in the method of Tauc [12]). A plot showing the measured band gap versus scandium concentration is given in Figure 1. A clear linear relation can be seen with optical band gaps lying between 2.5-4.0 eV. XRD showed very weak, if any, diffraction suggesting the films are amorphous or microcrystalline. The failure of the films to fully crystallize is consistent with our highest attainable growth temperature (~400 ^{o}C), which is below that needed to grow crystalline films [10,11].

It must be noted that this procedure is only approximate for these materials since they are amorphous/microcrystalline. The band tailing, which occurs in amorphous materials, results in a gradual increase in absorption at the band edge as compared to the sharp transition seen in crystalline materials. Tauc plots of amorphous materials show a characteristic tail region followed by a linear region. Since the fits were made to the largest linear region, the optical band gap energy was shifted toward higher energies (as seen in Figure 1). It is estimated that the shift to higher energy is ~0.5 eV. Thus the corrected range of the optical band gaps would be ~2.0-3.5 eV.

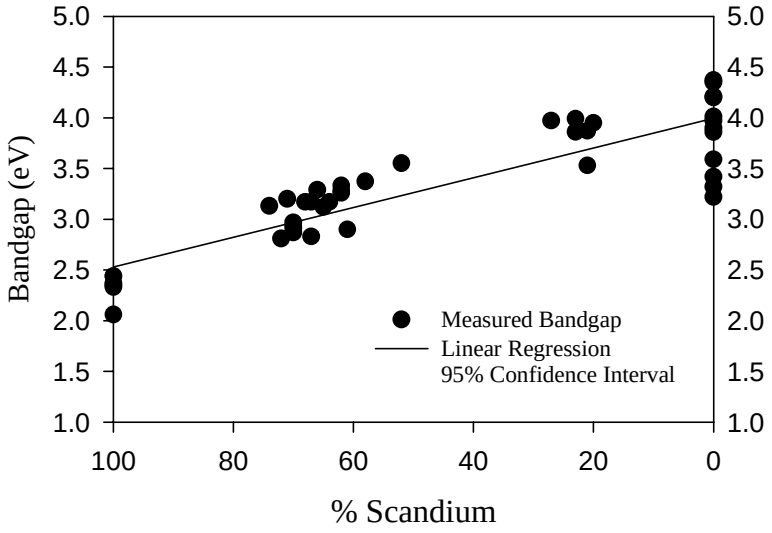

FIGURE 1. *Optical bandgap versus Sc concentration.*

VASE ellipsometry was used to investigate the material optical properties. Figure 2 shows typical ellipsometry data with fits (used to generate optical constants) included. The optical band gap determined from VASE ranged between 2.33 eV for pure ScN to 3.40 eV for pure GaN and also showed a linear dependence on alloy composition. The material optical constants *n* and *k*, for alloys of different composition, are shown in Figures 3 and 4 respectively.

The values for ScN and GaN are in good agreement with published results [4,13]. The films show an increase in *n* with increasing Sc concentration. A peak in *n* is seen around concentrations of about 50%. Further investigation is necessary to determine if this peak is due to an alloy property or from elsewhere (such as growth conditions or sample preparation). The extinction coefficient *k* remained low and relatively constant in the below gap region. The curve for GaN shows an increase in *k* for low energy, which could be due to absorption from mid-gap states associated with defects in the amorphous material; however, the exact origin of this absorption is not known.

Bilayers of ScN and GaN were grown to compare their absorption curves to those of the alloy films. Since ScN and GaN have different crystal structures, it was possible that a heterogeneous mixture was being grown instead of an alloy. Absorption from the bilayer films revealed a distinct feature absent in the alloyed films (see reference 9 for details). This was taken as evidence that the $Sc_xGa_{1-x}N$ films were alloys and not heterogeneous mixtures.

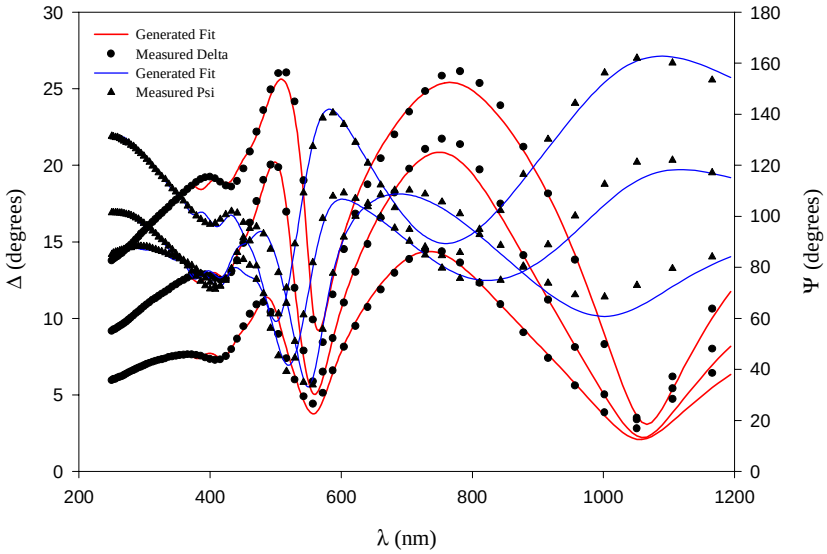

Figure 2. *Typical ellipsometry data. Measurements were made at 62, 67, and 72 degrees. Points are measured data; solid lines are generated fits from the Lorentz oscillator model.*

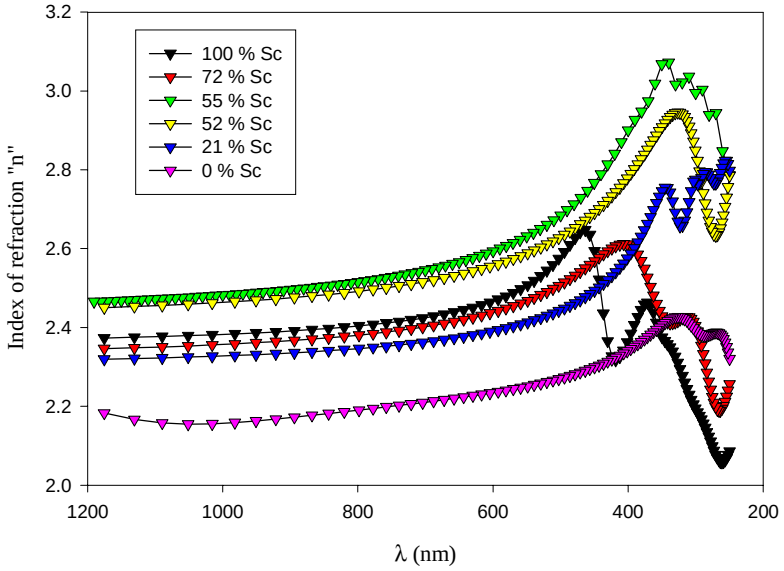

Figure 3. *Index of refraction 'n' in the region below optical absorption. Data generated from variable angle spectroscopic ellipsometry.*

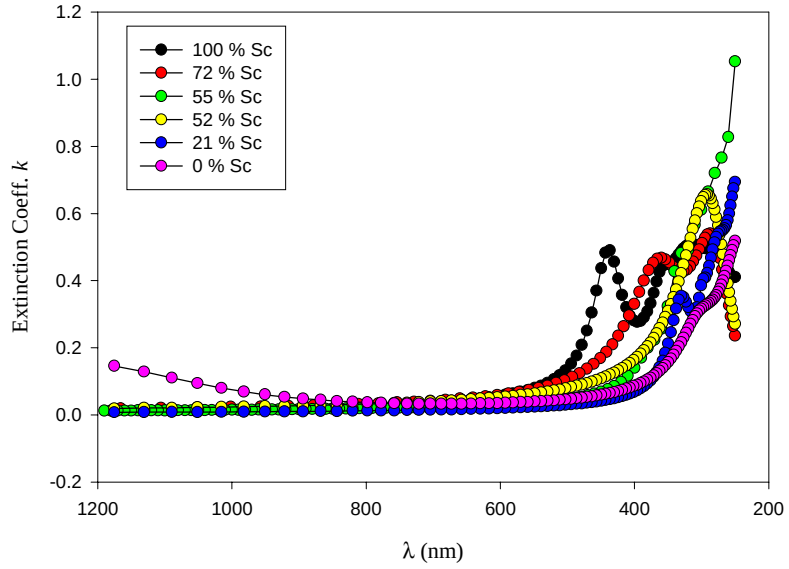

FIGURE 4. *Extinction coefficient k generated from VASE data for several different alloy compositions.*

4. Conclusions. Alloys of amorphous or microcrystalline $Sc_xGa_{1-x}N$ may be produced by reactive sputtering in the temperature range 300-675K. Direct measurement of the optical absorption revealed that the films have an optical band gap of ~ 2.0-3.5 eV. The band gap varies linearly with alloy concentration. Variable angle spectroscopic ellipsometry was used to verify the optical absorption as well as give the material optical constants in the range 250-1200 nm. Index of refraction, *n*, was found to be between ~2.0-3.1, while the extinction coefficient was found to be less than 1.2 for all materials.

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